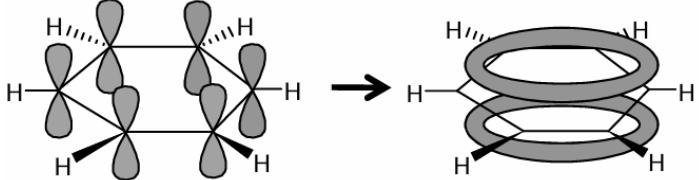


# Topic 18: Organic Chemistry – Arenes

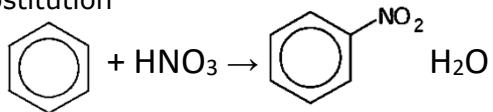
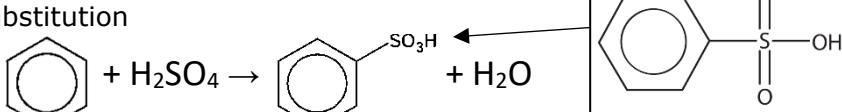
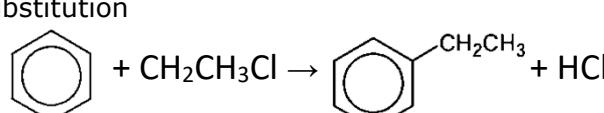
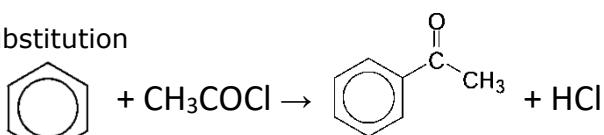
Knowledge of the common uses of organic compounds mentioned in this topic is expected.

**Students will be assessed on their ability to:**

<b>18.1</b>	<p>be able to use thermochemical, X-ray diffraction and infrared data as evidence for the structure and stability of the benzene ring</p> <p><i>Students may represent the structure of benzene as</i></p> <div style="text-align: center;"></div> <p><i>as appropriate in equations and mechanisms.</i></p>								
	<p style="text-align: center;"><b>Organic Compounds</b></p> <div style="display: flex; justify-content: space-around; align-items: center;"><div style="text-align: center;"><p><b>Aliphatic</b> (Non-cyclic/ Open chain) straight or branched chain hydrocarbons</p></div><div style="text-align: center;"><p><b>Aromatic</b> (Arene/ Closed Chain) hydrocarbon ring with delocalized electrons forming pi bonds in the ring</p></div></div> <p><b>!Benzene belongs in the aromatic class</b></p> <p><b>Benzene's Structure</b></p> <ul style="list-style-type: none"><li>- Simplest arene is benzene (molecular formula C<sub>6</sub>H<sub>6</sub>)</li><li>- Basic structure is six C atoms in a hexagonal ring, with one H atom bonded to each C atom</li></ul> <div style="text-align: center;"></div> <p><i>A little backstory on how we arrived at this new model of structure and stability of the benzene ring</i></p> <p><b>Problem 1: Shouldn't benzene decolourise bromine water in an addition reaction if it has C=C double bonds?</b></p> <p>Ans: There are no individual C=C bonds, so no reaction with bromine</p> <p><b>Problem 2: Shouldn't there be 4 isomers of C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub> according to Kekulé structure?</b></p> <p>Ans: There are only three because when the Br atoms are on adjacent atoms, there is no difference in the arrangement of electrons between these atoms</p> <p><b>Problem 3: Evidence from X-ray diffraction about the lengths of covalent bonds in molecules suggests that the carbon-carbon bonds in benzene are all the same, why?</b></p> <p>Ans: <table border="1" style="display: inline-table; vertical-align: middle;"><thead><tr><th>BOND</th><th>BOND LENGTH/pm</th></tr></thead><tbody><tr><td>C–C in cyclohexene</td><td>154</td></tr><tr><td>C=C in cyclohexene</td><td>134</td></tr><tr><td>C–C in benzene</td><td>139</td></tr></tbody></table> The bonds are the same length as they are identical Electrons are evenly distributed throughout the ring Kekulé structure would have shorter double bonds (C=C) and longer single bonds (C–C)</p> <p><b>Problem 4: Evidence from thermochemical data about enthalpy changes of hydrogenation suggests this diagram, why?</b></p> <p>Ans: When charge is spread across in a species, there is increased stability, which explains the 152kJ/mol greater stability of benzene compared with cyclohexa-1,3,4-triene</p> <div style="text-align: right; margin-top: 20px;"></div> <p><b>Problem 5: Evidence from infrared spectra of cyclohexene and benzene</b></p> <p>Ans: IR spectrum of benzene has a very strong absorption at 1500 cm<sup>-1</sup> which is typical of C=C in an aromatic compound (Absorptions for C=C in non-aromatic compounds are between 1680 and 1645 cm<sup>-1</sup>)</p>	BOND	BOND LENGTH/pm	C–C in cyclohexene	154	C=C in cyclohexene	134	C–C in benzene	139
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C–C in benzene	139								

	Arenes have high melting points due to the high stability of the delocalised benzene ring, but low boiling points as they are non-polar molecules and generally cannot be dissolved in water	
<b>18.2</b>	understand that the delocalised model for the structure of benzene involves overlap of p-orbitals to form π-bonds	
	<p><b>Delocalized Model for Structure of Benzene</b></p> <ul style="list-style-type: none"> <li>- Each C atom is bonded to two other C atoms and one H atom by single covalent sigma-bonds which leaves one delocalised electron on each C atom in a p-orbital, perpendicular to the plane of the ring</li> <li>- The six delocalized electrons in p-orbitals overlap in a ring structure above and below the plane of carbon atoms to form pi-bonds</li> <li>- Benzene is a <i>planar molecule</i> (The evidence suggests all the C-C bonds are the same and have a length and bond energy between a C-C single and C=C double bond)</li> </ul> 	
<b>18.3</b>	understand why benzene is resistant to bromination, compared to alkenes, in terms of delocalisation of π-bonds in benzene compared to the localised electron density of the π-bond in alkenes	
	Benzene <i>does not generally undergo addition reactions</i> (bromination addition) <ul style="list-style-type: none"> <li>- This is because these would involve breaking up the delocalised system (the delocalization of pi-bonds) unlike in alkenes where the electron density of the pi-bonds is localized</li> <li>- Hence, most of benzene's reactions are substitutions of one H for another atom or group of atoms</li> <li>- And since benzene has a high electron density and so attracts electrophiles, it mostly undergoes electrophilic substitutions</li> </ul>	
<b>18.4</b>	know the following reactions of benzene, limited to: <ol style="list-style-type: none"> <li>oxygen in air (combustion to form a smoky flame)</li> <li>bromine, in the presence of a catalyst</li> <li>a mixture of concentrated nitric and sulfuric acids</li> <li>fuming sulfuric acid</li> <li>halogenoalkanes and acyl chlorides with aluminium chloride as catalyst (Friedel Crafts reaction)</li> </ol>	
i	<p><b>Reactions with oxygen (Combustion)</b></p> <p>Benzene + Oxygen → Carbon Dioxide + Water</p> $\text{C}_6\text{H}_6(\text{l}) + 7.5\text{O}_2 \rightarrow 6\text{CO}_2 + 3\text{H}_2\text{O}$ <p>Benzene will burn in a smoky/ sooty flame</p> <p>The lower the carbon to hydrogen ratio, the sootier the flame</p>	<p><b>Test for aromatic compounds</b></p> <p>smoky flames indicate a positive test</p>
ii	<p><b>Halogenation of Benzene</b></p> <p>Mechanism: Electrophilic substitution</p> <p>Change in functional gp. <b>Benzene</b> + Br<sub>2</sub> → <b>Bromobenzene</b></p> <p>Reagents: FeBr<sub>3</sub> catalyst (or AlBr<sub>3</sub>)</p> <p>Conditions: Heat under reflux with halogen carrier (catalyst)</p>	<p>Same for reaction with chlorine (catalyst can be AlCl<sub>3</sub> or FeCl<sub>3</sub>)</p>

FeBr<sub>3</sub> can be made by reacting Fe with Br<sub>2</sub>

iii	<p><b>Nitration</b></p> <p>Mechanism: Electrophilic substitution</p>  <p>Change in functional gp. <b>Benzene</b> <b>Nitrobenzene</b></p> <p>Reagents: Conc. <math>\text{HNO}_3</math> in presence of conc. <math>\text{H}_2\text{SO}_4</math> (Catalyst)</p> <p>Conditions: Warm with reagents and catalyst at 50-60°C</p>
iv	<p><b>Sulfonation</b></p> <p>Electrophile: <math>\text{SO}_3</math> (fuming <math>\text{H}_2\text{SO}_4</math> is <math>\text{SO}_3</math> dissolved in conc. <math>\text{H}_2\text{SO}_4</math>)</p> <p>Mechanism: Electrophilic substitution</p>  <p>Change in functional gp. <b>Benzene</b> <b>Sulfonated benzene</b></p> <p>Reagents: Fuming concentrated <math>\text{H}_2\text{SO}_4</math></p> <p>Conditions: Heat under reflux at 40°C for at least 30 minutes (several hours)</p>
v	<p><b>Friedel-Crafts Reactions</b></p> <p>Type: Alkylation</p> <p>Mechanism: Electrophilic substitution</p>  <p>Change in functional gp. <b>Benzene</b> <b>Alkylbenzene</b></p> <p>Reagents: RCl (chloroalkane) in presence of anhydrous <math>\text{AlCl}_3</math> catalyst</p> <p>Conditions: Heat under reflux</p> <p>Type: Acylation</p> <p>Mechanism: Electrophilic substitution</p>  <p>Change in functional gp. <b>Benzene</b> <b>phenylethanone</b></p> <p>Reagents: Acyl chloride in presence of anhydrous <math>\text{AlCl}_3</math> catalyst</p> <p>Conditions: Heat under reflux (50°C)</p>

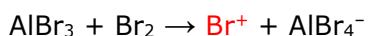
**18.5**

understand the mechanism of the electrophilic substitution reactions of benzene in halogenation, nitration and Friedel-Crafts reactions, including the generation of the electrophile

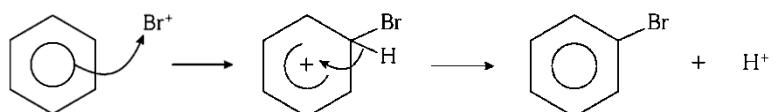
### **Electrophilic Substitution Mechanism**

#### **Halogenation**

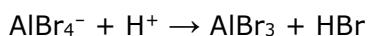
Step 1: Formation of the electrophile



Step 2+3: Electrophilic attack + Formation of the aromatic product



Step 4: Regeneration of the catalyst



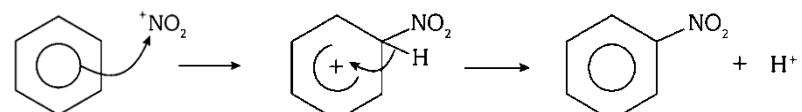
This reaction is done at 60°C.  
On using higher temperatures  
a second nitro group can be  
substituted onto different  
positions on the ring

#### **Nitration**

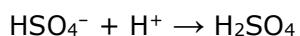
Step 1: Formation of the electrophile



Step 2+3: Electrophilic attack + Formation of the aromatic product

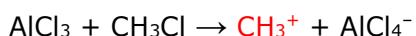


Step 4: Regeneration of the catalyst

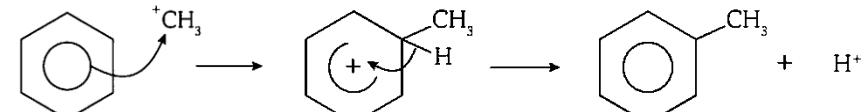


#### **Alkylation**

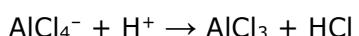
Step 1: Formation of the electrophile



Step 2+3: Electrophilic attack + Formation of the aromatic product

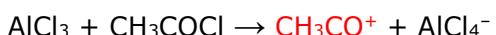


Step 4: Regeneration of the catalyst

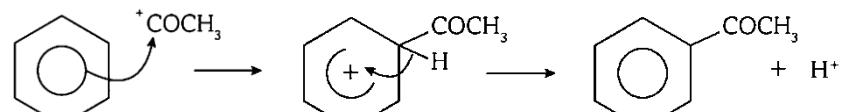


#### **Acylation**

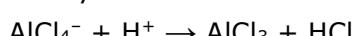
Step 1: Formation of the electrophile



Step 2+3: Electrophilic attack + Formation of the aromatic product



Step 4: Regeneration of the catalyst

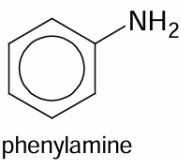
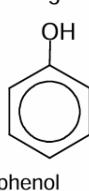
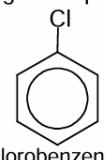


#### **Effect of side groups on benzene ring**

- Electron releasing side groups such as alkyl groups, phenols and amines releases electrons into the delocalised system and so increasing the electron density in the ring and making it more attractive to electrophiles
- Hence, their substitution reactions occur more readily with milder conditions

### Effect of delocalisation on side groups with lone pairs

If a -OH group, a Cl atom or an NH<sub>2</sub> group is directly attached to a benzene ring the delocalisation in the benzene ring will extend to include the lone pairs on the N, O and Cl. This changes the properties and reactions of the side group



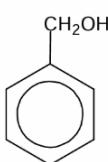
The C-Cl bond is made stronger. Typical halogenoalkane substitution and elimination reactions do not occur. Also the electron rich benzene ring will repel nucleophiles

Delocalisation makes the C-O bond stronger and the O-H bond weaker. Phenol does not act like an alcohol - it is more acidic and does not oxidise

Less basic than aliphatic amines as lone pair is delocalised and less available for accepting a proton

### 18.6

understand the reaction of phenol with bromine water and the reasons for the relative ease of this reaction compared to benzene



This is not a phenol, but is an alcohol because the OH group is attached to an alkyl group rather than the benzene ring.

### Phenols

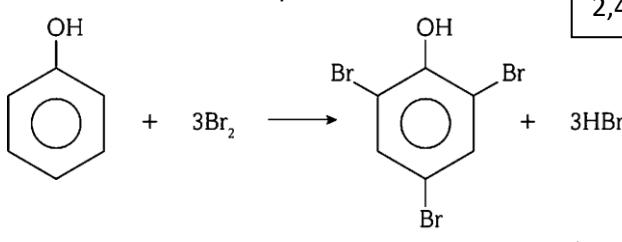
- A phenol consists of a hydroxy (-OH) group directly attached to a benzene ring (Note that the -OH group should be attached to the benzene ring and not an alkyl group, to be considered as a phenol)
- Phenols are very weakly acidic (They are weaker acids than carboxylic acid)
- Both phenols and carboxylic acids will react with Na metal and NaOH
- Only carboxylic acids will react with Na<sub>2</sub>CO<sub>3</sub> as a phenol is not strong enough an acid to react

### Bromination of Phenol (Test for phenol)

Reagents: Bromine water

Type: Electrophilic substitution

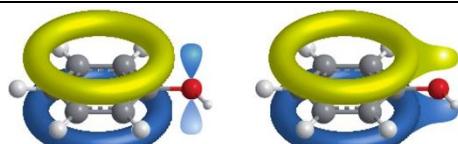
Conditions: Room temperature



**Phenol decolourises the orange bromine solution to form a white precipitate of 2,4,6-tribromophenol**

Compared to bromination of benzene,

- Phenol does not need a catalyst, occurs at room temp. (no need to be heated under reflux) and undergoes multiple substitution (3 substitutions)
- The lone pair of electrons on the oxygen in phenol overlaps with the delocalised pi electron system of the benzene ring, increasing its electron density and making it more susceptible to electrophilic attack



**fig A** The electrons in the p<sub>z</sub>-orbital of the oxygen atom become part of the delocalised electron system. This increases the electron density above and below the ring and makes the molecule more attractive to electrophiles such as Br<sup>+</sup>.

Phenols are used in the production of plastics, polymers, antiseptics, disinfectants and resins for paints

### Further suggested practical:

Carry out the reactions in 18.4, and 18.6 where appropriate (using methylbenzene or methoxybenzene)